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"Non Linear Current in a Plasma"

"Aeropalynological Survey in the Lower Atmosphere in the Mid-Pacific Region"

"Synthesis and Physical Chemical Properties of New Metal Acetylacetonates Polymers"

(Elementary Particles)
(I) Statistical Theory of Macromolecules
(II) Studies of Metal Solutions

"X-Ray Investigations"

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Final Progress Report
NGL 33-001-001

March 1, 1963 to August 31, 1970

SUMMARY OF PROGRESS

Since the inception of the grant in 1963, twenty research projects in the departments of Biology, Chemistry and Physics have received support. The individual research projects are listed in this report. A total of twenty-five students. twelve undergraduate, nine Ph.D. and four M.S. level students have received some support under the grant. A total of twenty-four publications has resulted from the research under the grant. The grant was administered by a committee with one representative from each of the three major departments involved, with the principal investigator acting as administrator with the assistance of secretarial services provided under the grant. In general, three or four major projects. and an equal number of minor (in terms of grant support) projects were supported at any given time. In addition, technical support facilities were also assisted with grant funds. The grant enabled the scientific research programs at Adelphi University to improve considerably.

For a summary of major technical progress accomplished under the grant, refer to the reports of Bettelheim, Genberg, Gillespie, Dooher, Lemos, Moon, Morrone and Zajac in the individual reports that follow.

Edward A. Burke Principal Investigator TITLE: Physical Chemical Properties of New Silicon Compounds

PRINCIPAL INVESTIGATOR: F. A. Bettelheim

Department of Chemistry

DESCRIPTION:

During the last 5 years a number of new silicone polymers were synthesized in my laboratory with the definite purpose of achieving thermally stable (low and high temperature range) and mechanically suitable (desired range of elastic, storage and loss moduli) group of polymers.

The summary of the work can be divided into three groups of compounds:

The triazinyl ethers were prepared by a number of techniques. The best results were obtained when the siloxane diols were dissolved in dimethylformamide and stoichimetrically variable quantities of cyanuric chloride dissolved in dioxane was added. Base catalyst, mainly KOH was added either in the solid form or in water. This served also the purpose to neutralize one of the reaction products, HCl. Small quantities of dimethylsulfoxide were used as promoter.

In preparing thermally stable new silicone polymers, the effect of the incorporation of a triazine ring in the siloxane chains were investigated. To that effect polysiloxane chains

were polymerized with base catalysis. Dimethyl-(M), diphenyl-(P). bis (p-chlorophenyl) - (CP) and bis (3.4-dichlorophenyl-(DCP) siloxanes were prepared as reported before. Copolymer siloxane chains of M-P, M-CP, M-DCP, P-Cp, P-DCP and CP-DCP were prepared in 1:2, 1:1 and 2:1 ratios also by base catalysis. Similarly block copolymers of the same were prepared. Elementary analysis and infra-red spectroscopy were used to confirm the composition of the products. On the average, a degree of polymerization 8-10 was achieved in the final products which varied in consistency from oily (methylsilicone) to resinous and solid as the proportion of P, CP and DCP increased. Especially copolymers and block copolymers of CP and DCP with M and P yielded products which settled into two phases; (a) an insoluble solid, and (b) soluble resin. On the basis of analysis and infrared spectra, one could identify the insoluble solids as containing predominantly CP and DCP monomers and probably crosslinked after a certain amount of cleavage of the siliconphenyl bond. The soluble resin contained also CP and DCP building blocks but in lesser quantities than the original reaction mixture.

The triazinyl ether formation occurred best with DCP diols and in decreasing order with CP, P and M. diols. Under certain conditions (aqueous ethanol with NaOH and toluene solvents), the diol of a dimethylsiloxane reacted with cyanuric chloride to give a water soluble compound of low molecular weight in which apparently a quaternary ammonium salt was formed rather than the triazinyl ether. The success of the ether formation was apparently determined by the inductive effect of the side chain of the siloxanes. Hence, in forming the thermally stable and insoluble triazinyl ethers with the different copolymers and block copolymers enumerated above, we made a practice to react the cyanuric chloride with 3 equimolar P, CP or DCP diols first at moderated temperatures up to 80°C for 5-10 minutes and then adding the

prepared copolymers and block copolymers in the desired proportion. Chlorine analysis of the final product indicated that in no case did we achieve 100% condensations and under the best conditions about 15% of the chlorine in the cyanuric chloride remained unreacted. The replacement of chlorine on the s-triazine nucleus has been found to occur in stepwise fashion being both temperature dependent and influenced by the nature of the substituent. Our experiments indicated that the DCP was the best substituent for the replacement of chlorine but at the same time extensive phenyl cleavage occurred.

The structure of the new compounds synthesized were studied by elementary and convential chemical group analyses; infra-red spectroscopy and NMR spectroscopy. The thermal properties have been measured by thermgravimetric analysis and the solid state structure have been studied by X-ray diffraction.

B) Poly (-s-triazine-R-siloxane) where R can be methyl, phenyl,-chlorophenyl and dichlorophenyl.

C1
$$\begin{pmatrix} C_1 \\ N \\ N \\ N \\ C_1 \end{pmatrix}$$
 + 3 Mg + 3 C1-Si-R₂ $\frac{THF}{R_1}$ $\frac{R_1}{R_1}$ $\frac{R_1}{R_2}$ + 3 Mg C1₂ $\frac{R_1}{R_1}$ $\frac{R_1}{R_2}$ $\frac{R_1}{R_1}$ $\frac{R_1}{R_2}$ $\frac{R_1}{R_1}$ $\frac{R_1}{R_1}$ (11)

In our first attempt the R_1 and R_2 groups were -CH₃ groups but other polymerization reactions were done with

$$R_1 = CH_3$$
, $-C_6H_5$, $-C_6H_4C1$, $-C_6H_3C1_2$ and $R_2 = Et0$ - or Me0-

The basic premise of this reaction is the formation of the Gringnard reagent of ${}^{c}_{3}{}^{N}_{3}{}^{c}_{1}{}^{c}_{3}$ in the presence of dimethylchlorosilane. The formation of the di-Grignard is more likely than the formation of the tri-Grignard; therefore, the disubstituted species should be more predominant. The I.R. spectra of the product indicates the presence of the triazine ring, Si-CH $_{3}$ and Si-H. The U.V. also shows the presence of the triazine ring in the product. The emission spectra definitely proves the presence of Si, but it also shows the presence of Mg.

This is a <u>first</u> since Grignards of cyanuric chloride (IV) have not been isolated as yet. We have succeeded in making this compound; and further studies have been conducted to purify it from the by-products, such as coupling products of the triazine ring itself.

The next step in our synthesis of new thermally stable polymers is the formation of the silanol. This is accomplished by reacting the product of Reaction 2 with peroxybenzoic acid forming:

The final step in the formation of poly (hexamethyl-siltriazyl-siloxane) is the polymerization of the silanol V which is accomplished in the following ways:

- 1. refluxing in an inert solvent
- 2. refluxing in an inert solvent with a catalyst.

The final product is a crosslinked polymer of high thermal properties.

A comparative study of the thermal and mechanical properties of our poly(s-triazine methyl siloxane) vs siloxane copolymers have been conducted. The T.G.A. and DTA techniques both indicate much greater thermal stability of the poly (s-triazine methyl siloxane) than the siloxane copolymers.

The mechanical properties of the poly-s-triazine methyl siloxane polymers gives dispersion and absorption curves similar to amorphous type polymers. The most remarkable dispersion is seen in the region of the glass transition. The storage modulus E falls from the glassy state to the soft rubber and a sharp large absorption appears. This absorption mechanism is due to the initiation of the micro Brownian motion of the modular chains from the frozen state.

C) The third group of new silicone polymers is given in reaction 3.

This reaction leads to the formation of the monomer. This monomer can be hydrolyzed and polymerized similar to the chlorosilanes. Therefore, we can homopolymerize VI or Copolymerize VI with other silicons. R is cyclic and aromatic; R' and R" are CH_3 , phenyl and chlorophenyl.

The characterization entails: (1) Light scattering for molecular weight and R_{G} ; (2) Osmotic pressure - number average molecular weight, and dependence of the second virial coefficient on solvent and temperature; (3) Thermal properties - TGA, DTA, DTGA; (4) Mechanical relaxation using the Vibron.

D) A fourth project of studying organized superstructures in gels of polymers by light scattering has been successfully completed.

PUBLICATIONS:

- 1. F. A. Bettelheim, W. Wood and R. D'Amelia, Proc. Internatl. Symp. on Macromolecular Chem., Tokyo, <u>II</u>, 82, (1966).
- 2. F. A. Bettelheim and R. D'Amelia, J. Polymer Sci. C <u>23</u>, 409, (1968).
- 3. F. A. Bettelheim, J. Polymer Sci., A2, 5, 1043, (1967).
- 4-5. R. D'Amelia and F. A. Bettelheim, Submitted to the J. of Polymer Sci.

STUDENT SUPPORT:

Mr. D'Amelia was supported by the Multidisciplinary grant throughout his graduate studies. He has received a M. S. degree in 1967 and he will receive his Ph.D. degree in 1971.

TITLE: Analysis of Biological and Ecological Systems in Non-equilibrated Environments.

PRINCIPAL INVESTIGATOR: Harry Brenowitz and Ronald Wilson Department of Biology

DESCRIPTION:

Diurnal, seasonal and yearly variations of temperature, salinity, pH, dissolved oxygen, and changes in the numbers, kinds and activities of indigent and transit populations of primary producers and primary consumers in Great South Bay were begun in the spring of 1963.

The 1964 data clearly indicated lower productivity when compared with the 1963 data. This was probably due to the fact that salinities had increased considerably resulting in less than optimum conditions for the dominant producer organisms. This further indicated that the bay was a disturbed ecological system. Theoretically, a complex mature ecosystem would have in reserve, species which would grow under a wide variety of ecological conditions. The inherent instability of a system dependent on a single producer species was demonstrated by the 1963 and 1964 data.

The work in 1965 was a continuation of the study of complex interralationships between endemic populations of a disturbed ecosystem and extended to include studies on specific flow patterns of the dominant species populations at the various trophic levels whthin the system. Laboratory studies on the utilization of the marine alga, Nannochloris in the nutrition of the economically important clam, Mercenaria mercenaria were begun. These experiments indicated that the clam does not use Nannochloris as a food source. The work on the economically important bay scallop, Pecten irradiens was not completed.

However, the preliminary data indicated that like the clam, the scallop did not utilize <u>Nannochloris</u> as a food source. Similar experiments on the copepods, the chief component of the primary consumers were not completed. However, the preliminary data seemed to indicate that the copepods did not feed on the <u>Nannochloris</u>.

Field observations on the <u>Nannochloris</u> population indicated that they were present in insignificant numbers during the spring, summer and early fall. During the summer of 1965, the "small forms", mainly <u>Nannochloris</u> which had previously been present in insignificant numbers suddenly bloomed in several areas of the bay. Organisms in excess of $9.7 \times 10^6/\text{ml}$ were found at some of the stations sampled. The field and laboratory data seemed to bear out the idea that the primary producer <u>Nannochloris</u> can and does block energy flow to the higher trophic levels.

Thus, the 1963, 1964, 1965 studies indicated that the Great South Bay system was erratic and that the amount of photo-synthesis did not vary with the amount of radiant energy the system received as it normally does in other estauarine systems.

During 1965 and the early part of 1966 the diurnal oxygen studies continued for a series of seven stations in Great South Bay and four stations were added in South Oyster Bay. The analysis of the data on dissolved oxygen was not made due to the fact that the diffusion correction factor for Great South Bay was not determined. The use of diffusion correction factor utilized in other bay systems were not adequate for application to the Great South Bay System. The preparation of equipment and plans for determining the diffusion rates of oxygen and carbon dioxide at air/water interface were stopped due to the fact that the project was phased out of the NASA grant in the summer and fall of 1967. Other aspects

of the research begun in 1966, namely Benthic studies, Zooplankton studies, and further studies on the utilization of Nannochloris in the nutrition of the clam, Mercenaria mercenaria were not completed due to the plans to phase this research out of the multidisciplinary research program. Thus, the major and minor thrusts of the project were not completed and to date no publications have been released.

The student support during the period the research was funded is summarized below:

- 9 Undergraduates 9 B.S.'s, 7 continued studies toward graduate degrees.
- 1 Graduate students 2 MS's

TITLE: Effects of Varying Physical Parameters on Post Irradiated Bacterial Cells

PRINCIPAL INVESTIGATOR: Concetta B. Cabral Department of Biology

DESCRIPTION:

In the background of the major aspects of the problem has been the continuation of a long series of techniques capable of the isolation and identification of ancestral and aberrant forms of the test organism being investigated; this has been accomplished in conjunction with the adoption of basic staining and cultural techniques tested and proven to be advantageous in the growth and in the examination of the test organism.

Optimal procedures regarding each of the following aspects pertaining to the problem have now been determined:

Most efficient quantitative determinations for the nutrient broth cultivation of the test organism: (2) Most efficient quantitive estimations of bacterial growth exposed to diverse environmental conditions; (3) Maximum efficiency of our U-V unit in modifying survival and mutational statistics in terms of U-V intensity and integrated intensity; (4) Most productive solid medium for auxotrophic and prototrophic strains of the test organism; (5) The organization of a definitive series of tests to be used routinely in the determination of cultural, morphological, and physiological modifications of the test organism pursuant to and following exposure to ultra-violet radiation; (6) Determinations of the optimal times in the growth cycle of the test organism (as we have found between the 15th and 16th hour following incubation rather than after the traditional 24 hour incubation period) when tests could be performed most efficiently and productively; (7) improvement in techniques relating to the isolation and examination of "delayed mutants"; (8) The

devisement of methods essential in ascertaining the <u>precise</u> <u>time</u> marking the termination of the period of susceptibility of the test organism to post-irradiational environmental influences as well as the experimental conditions necessary to elucidate this fact; (9) The devisement of methods to determine <u>most rapidly</u> and efficiently the distribution of variants into (a) spontaneously-induced ones, (b) experimentally-induced ones, and/or; (c) naturally-selected ones; (10) Methods for determining whether initial variants are irreversible.

Some of the specific procedural techniques tested and now adopted are: (1) plating at high dilutions to determine survival rates wherein typically 0.1 ml of culture is diluted to 1 to 10⁻⁶; (2) plating at lower dilutions to determine mutational rates; (3) substitution of dilution fluid (25 ml. of nutrient broth added to one liter of 0.9 Nacl) in place of saline un-enriched by nutrient broth, the former allowing for maximal recovery of cells; (4) cultivation of the test organism (prototroph) in minimal medium designated as 50 X E, which is a salt solution containing principally citric acid, potassium phosphate, magnesium sulfate, and sodium ammonium phosphate added in precise quantities.

TITLE: Collision Processes in Gases

PRINCIPAL INVESTIGATOR: D. E. Cunningham - Department of Physics

DESCRIPTION:

In order to better understand the nature of the effect which is used to determine atomic collision cross sections of various gases, thereby obtaining insight into energy transfer processes in the upper atmosphere, foreign gases were mixed with irradiated mercury vapor at pressures such that the time between collisions was roughly of the same order as the lifetime of the (particular) excited state of mercury. The technique which was used involved the measurement of differences in observed emission characteristics as a function of pressure of the foreign gas introduced into a cell containing the mercury vapor which was optically pumped with radiation at 2537A. The change in the character of the emitted radiation and the decrease in intensity of the emitted radiation with changes in pressure of the foreign gas was used to determine the effectiveness of the collision process, hence the atomic collision cross section, for energy transfer. This technique is described in greater detail in (1) and (2).

It was reported in (1) that the "lifetime" of the excited state is not single-valued, but rather (due to an apparent coherent photon absorption process³) is lengthened as the temperature of the cell, hence pressure, is increased.

REFERENCES:

- (1) Adelphi University Research Report, NASA grant NsG 394.
- (2) D. E. Cunningham and L.O. Olsen, Phys. Rev. <u>119</u>, 691 (1960).
- (3) P.J. Barrat, Le Journal de Physique and Le Radium 20, 42 (1959).

PUBLICATIONS:

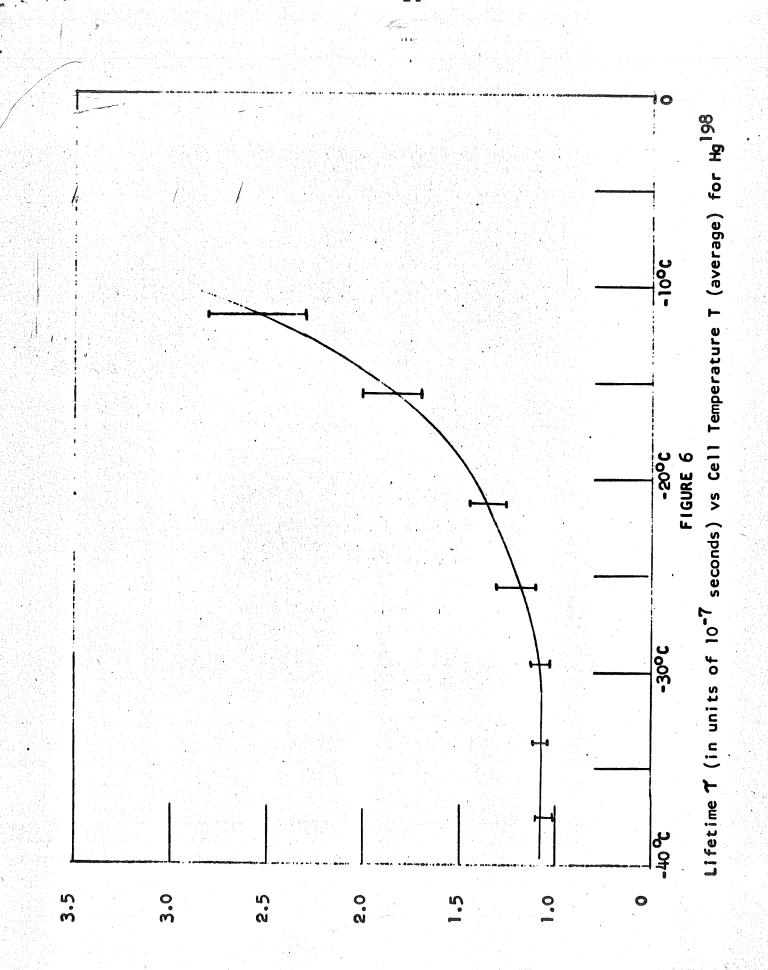
Adelphi University Research Report NASA grant NsG-394.

SUMMARY OF FINDINGS:

- 1. The character and intensity of the emitted radiation is sensitive to the pressure of the foreign gas.
- 2. The "lifetime" of the 6^3P_1 state in mercury is not single-valued but was found to change by a factor of 3 in the temperature, hence pressure, range investigated.
- 3. It has been possible to fit all the polarization vs. magnetic field data (the Hanle method of determining atomic excited state lifetime) with a single value of excited state lifetime in spite of the variation mentioned previously.

<u>\$TUDENT SUPPORT</u>: (Undergraduate)

- 1. Ed Fraser
- 2. Fred Helm



(I)
TITLE: Electromagnetic Form Factors of Hadrons

PRINCIPAL INVESTIGATOR: John Dooher - Department of Physics

DESCRIPTION:

The electromagnetic properties of the strongly interacting particles (hadrons) are described by the introduction of form factors which determine such physical quantities as the charge radius of the proton, hand care effects in proton and neutron structure, and other quantities relevant to the study of the structure of elementary particles. These form factors also determine the high energy behavior of cross sections for processes involving photons (virtual or real) and hadrons which are useful in astrophysical studies (e.g. electron-proton scattering).

It is important therefore to have sufficient theoretical understanding of these form factors to enable one to calculate them for various processes. Calculations have been completed which indicate that these form factors satisfy unsubtracted dispersion relations in the relevant variables. Also, as a result of this calculation it may be concluded that in many cases the form factors can be approximated within a reasonable degree of accuracy by expression of the following form.

$$F(x) \sim \frac{c}{x^2 + m^2}$$

where C and m^2 are constants.

It is possible to derive sum rules of the form $a = \int F^2(x) dx$ where a is a known quantity. This enables one to determine C and m^2 . In order to derive these sum rules we assume a few simple algebraic relationships among the components of the electromagnetic and weak hadron currents.

TITLE: Spectral Sum Rules and High Energy Behavior of Form Factors. - John Dooher

DESCRIPTION:

Sum rules were found which relate integrals over pseudoscalar and scalar spectral functions to integrals over axial vector and vector spectral functions. By the use of pole approximations, various relationships among decay amplitudes and coupling constants may be derived. Also information on high energy neutrino production processes such as $\mathcal{U} + \mathcal{U}$ (e) hadrons (strongly interaction particles) may be derived.

The question of the mixing of various vector meson states has been considered and by use of the Gell-Mann current commutation relations, a non perturbative treatment of this problem was developed which allows direct comparison with experiment of the mixing theory of M. Kroll, T. D. Lee and Bruno Zumino.

TITLE: Dynamical Sum Rules and the Zero Momentum Limit
John Dooher

A relationship between the zero momentum limit of vector meson decay amplitudes and the equality of the axial vector spectral integrals and the psuedoscalar spectral integrals was found. Taking this result as a bootstrap-like relation where the period meson is not composite, it is possible to calculate the vector meson masses and coupling constants in terms of pseudoscalar meson parameters. It is also possible to test vector meson saturation of spectral sum rules, thereby putting limits on the validity of global pole dominance. From this, it is possible to estimate hadron production by leptons at high energies which is useful both in accelerator and cosmic ray research.

(IV)

TITLE: Current Algebra Dynamics and "Quark" Hunting.

John Dooher

DESCRIPTION:

In the study of the dynamics of current algebra, the relationship between the phenomenological approach to low energy multi-pion process using model Lagrangians and the zero momentum limit approach using L S Z reduction techniques was elucidated. The results are encompassed in a series of sum rules. In summary, the results imply that SU₃ symmetry is exact for the pion and kaon decay amplitudes at zero momentum.

A study was also made of the feasibility of hunting for "quarks" in the cosmic radiation by use of satellites. By examining new methods of measuring the energy of a particle and its mass, it was possible to demonstrate the feasibility of such satellite experiments. The devices considered, utilize the transitron radiation emitted by a particle when it crosses a boundary and also use a photocalorimetric method of measuring the total energy of a hadron that has been absorbed in a chunk of heavy crystal.

<u>TITLE</u>: Magnetic Properties of Type II Superconductors

PRINCIPAL INVESTIGATOR: Richard W. Genberg - Department of Physics

DESCRIPTION:

Two types of superconductors are recognized with "type II" possessing typically a high current-carrying capacity, hence, type II superconductors should prove valuable in many practical applications. In order to obtain further insight into the fundamental properties of type II superconductors, we have investigated the magnetic properties of vanadium, one of the few elemental type II superconductors; the magnetic studies were conducted by examining the torque as a function of the magnitude of the applied field.

We have found in single crystalline specimens with the cylinder axis of the sample perpendicular to the applied field direction that: (1) the torque exists only in the superconducting state and it varies in a reproducible manner with the magnitude of the applied field, (2) the variation of the torque with applied field is orientation dependent. and (3) the torque is not generated as a result of the time rate of change of the applied field. Theoretical considerations $^{1-3}$ have indicated that the observed torque is attributable to magnetocrystalline and shape anisotropy effects, with the former arising from the inherent properties of the material and the latter from a lack of geometrical symmetry of the sample about the field direction. An analysis of the torque data has resulted in good qualitative agreement with theoretical predictions and a preliminary determination for vanadium of several parameters of type II superconductivity. these parameters were found to have the following values:4 $K_2 \approx 0.86$, $H_{c2} = 770$ gauss and $P \approx 10^{-5}$ where P represents

the effective mass anisotropy. A more reliable determination of these values can not be completed at this time as the theory for magnetocrystalline anisotropy for the case of cubic crystalline structure (that of vanadium) is incomplete. In addition, this technique appears capable of resolving $H_{\rm c2}$ with considerable precision, hence, should not only yield reliable $H_{\rm c2}$ values but its angular variation as well.

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- 1. G. L. Dorer and H. E. Bommel, Phys. Rev. <u>183</u>, 528 (1969).
- 2. J. A. Cape and J. M. Zimmerman, Phys. Rev. <u>153</u>, 416 (1967).
- 3. J. A. Cape, Phys. Rev. 179, 485 (1969).
- 4. These values for K_2 and H_{c2} are in good agreement with those of R. Radebaugh and P. H. Keesom, Phys. Rev. 149, 217 (1966), while the value for P is reasonable.
- 5. For a discussion of the anisotropy in $H_{\rm C2}$ see the paper by D. E. Farrell, B. S. Chandrasekhar, and S. Huang, Phys. Rev. <u>176</u>, 562 (1968) and references therein.

PUBLICATIONS:

- "Anomalous Magnetization of Elemental Type II Superconductors", E. Hecht and R. W. Genberg, Bull. Am. Phys. Soc. <u>13</u>, 730, (1968).
- 2. "Anomalous Magnetic Behavior of Superconducting Vanadium and Niobium", E. Hecht and R. W. Genberg, Jour. Appl. Phys. 39, 2159, (1968).
- 3. "Torque Measurements Performed on Bulk Superconductors", R. W. Genberg and E. Hecht, Bull. Am. Phys. Soc. <u>13</u>, 1456 (1968).
- 4. "Torque Studies Performed on Superconducting Vanadium", R. W. Genberg, Submitted to the Journal of Applied Physics.

SUMMARY OF FINDINGS:

- The measured torque on vanadium is in good agreement with that predicted by theory (as the theory of magnetocrystalline anisotropy is as yet incomplete, so is the comparison).
- 2.) Preliminary determinations of several parameters of superconducting vanadium have yielded values in good agreement with those of other investigators for samples of similar purity. In particular, at 4.2° K K₂ \approx 0.86, H_{C2} = 770 Oe., and P \approx 10⁻⁵ where P represents the effective mass anisotropy.
- 3.) The technique is capable not only of measuring $H_{\rm c2}$ but should yield a precise determination of the anisotropy of $H_{\rm c2}$.
- 4. Since null-deflection torque balances can be built with great sensitivity, this technique should prove useful in studying the magnetic properties of many if not all type II superconductors.

LIST OF ALL PROJECTS:

- 1. Magnetic susceptibility and magnetothermal oscillations in beryllium.
 - (Since the torsion balance to measure the magnetic susceptibility was completed but the samples of beryllium were never received, this project in effect was never carried out as no measurements were performed. Instead the equipment was utilized to measure the magnetic properties of superconductors).
- 2. Magnetic Properties of type II Superconductors.

STUDENT SUPPORT:

- 1. E. Hecht, Ph.D. Thesis (project was the magnetic properties of type II superconductors) (1965-1967).
- 2. R. Hembach, Doctoral student (1970-).

TITLE: The Effects of Some Physical Parameters on Biological Materials.

PRINCIPAL INVESTIGATOR: Ronald Gillespie
Department of Biology

DESCRIPTION:

Studies of the effects of ionizing radiation, hypobaric pressures, magnetic flux and hypothermia on biological parameters have been verified and expanded.

Animals (mice) subjected to stronger doses of ionizing radiation (400 roentgens versus previous levels of 300 and 350 roentgens) and/or hypobaric pressures (equivalent to an altitude of 10,000 feet) for 39 day periods showed greater alterations in blood lymphocytes than formerly found. There was an initial rise followed by a depression considerably below normal levels which continued throughout the experimental period. The combination of these two forces offers the possibility of controlling the level of this cell type so that the destructive effect of the radiation could be compensated by the lowered pressure. This may have important implications for animals (or humans) exposed for long periods to dangerous levels of radiation as well as for experiments such as tissue grafting which involve antigen-antibody reactions.

Other mice radiated as above and/or exposed to a magnetic flux of one kilogauss for 21 day periods did not present as clear cut a picture. There was however, a suggestion of a sex difference. Males did show a slight depression of lymphocytes below the normal levels when subjected to magnetism alone. Females showed no such effect. In all cases when the stresses were removed, the animals which were irradiated recovered to normal levels at a faster rate than when magnetism was a factor.

Hypothermia experiments to study electrolyte changes with isolated perfused rabbit hearts has confirmed the previous finding that there is an efflux of potassium ion as the temperature was lowered. This effect was re-

versed when the antifreeze agent dimethyl sulfoxide was present in the perfusing medium. Addition of another antifreeze agent (dimethylacetamide) had no such effect. Progressive cooling and rewarming of the tissue caused a corresponding efflux and influx respectively of the potassium ions. The levels of sodium and chloride remained unchanged in all experiments.

Other hypothermic experiments involving whole animals (rats) have been conducted to assess the effect of acute and chronic exposure to lowered temperatures on the plasma lipid levels. In all cases there was a significant increase in the free fatty acid fraction and no change in cholesterol and lipoproteins. With acute exposure no changes in phospholipid or triglyceride levels were noted but with the prolonged treatment there was a marked increase. These data suggest that free fatty acids, and to a lesser extent, triglyceride and phospholipid, are of primary importance in providing energy to combat cold stress.

TITLE: The Effects of Hypothermia and Dimethylsulfoxide on Rabbit Saliva.

PRINCIPAL INVESTIGATOR: Ronald Gillespie, and Malcolm E. Hair Department of Biology

DESCRIPTION:

The purpose of this investigation was to determine the status of Na^+ and K^+ in rabbit parotid saliva under conditions of lowered body temperatures and with the administration of DMSO intra-peritoneally.

Briefly, rabbit saliva was collected by means of a modified Lashley cup after secretion was stimulated by injection of pilocarpine. Whenever possible, samples of blood were taken so that plasma Na^+ and K^+ could also be measured. The concentrations of the electrolytes were measured on a flame photometer.

The results showed that K^+ concentrations in parotid saliva increased about two-fold over normal (24 meq/L vs. 12 meq/L) when the body temperature was depressed to 32° C or below (normal temperature =38°C). Cooling was effected by means of a combination of cooling blanket and ice-packs wrapped around the animal.

When DMSO was injected before cooling, salivary K^+ levels were found to be about 30 meq/L. Under all conditions salivary Na^+ remained within the normal range - 50-80 meq/L.

Plasma K⁺ levels appeared to rise slightly in the first phase of cooling but were somewhat depressed as the body temperature dropped. It is felt that there is a movement of K⁺ from active shivering muscles into the blood stream, from where some of it finds its way into salivary glands. The loss of water from saliva under hypothermia may also play a role in the elevated K⁺ levels found.

<u>TITLE</u>: The Biosynthesis and Degradation of Membrane Phospholipids

PRINCIPAL INVESTIGATOR: J. Y. Kiyasu - Department of Biology

DESCRIPTION:

During a two year period (1964-1966) investigations were conducted in three different areas relating to the biochemistry of living tissues.

- A) The first area was to investigate the role of phospholipids in cell membrane. It is well known that the physiological role of phospholipids is to provide an interphase between hydrophobic and hydrophilic regions by special orientation of the molecules, so that the polar head dips into the hydrophilic phase. Using membrane fragments of endothelio-reticulum of liver cells, we found direct correlation between the turnover of phosphorus in the membrane and the induction of membrane enzyme. The turnover of phosphorus was studied by radioactive tracer techniques and enzyme assays were conducted as a function of time. Other correlation was established between the phosphorus turnover rate and inorganic cation concentration, the latter may be necessary for the function of the induced membrane enzyme.
- B) The interactions between hydrophobic proteins (which are not soluble in water) and polysaccharide phosphates were studied. Glycogen phosphate and dextran phosphate was synthesized and the rate of solubilization of hydrophobic proteins in water was observed as polysaccharide phosphate was added. When the protein was made hydrophobic by denaturing in media which competes for water such as ethanol, methanol, etc., small quantities of the polysaccharide phosphates acted as solubilizing agents. Thus, these polysaccharide phosphates can be used as antidenaturing agents in certain environments.

C) In collaboration with Dr. R. J. Gillespie, studies were conducted on low temperature survival of animals. Cockroaches were cooled down to -150° C, survival was good down to -9° but not much below. Feeding antifreeze agents so that no ice crystals should form in the body liquids did not help the survival rate. As a matter of fact these agents proved to be quite poisonous.

The effect of radiation and magnetic field has been studied on mice. This project was conducted in collaboration with Dr. Genberg. While body weight showed no effect as a result of the radiation or magnetic field, the lymphocytes count increased with the dose of radiation.

TITLE: Oscillator Strength Calculation for TI⁺ in KCI, KBr and NaCl

PRINCIPAL INVESTIGATOR: Anthony M. Lemos - Department of Physics

DESCRIPTION:

The general research areas considered during my tenure under the NASA grant were the deep electron traps in alkali halide crystals. Specifically the problems surrounding the optical absorption and emission of the F- center and the KC1:T1 center were attacked and partially solved. The research is still in active progress. During this period, two men received their Ph.D's with the assistance of the NASA grant: Dr. Michael Stauber, 1968 and Dr. John Marion, 1970. A paper entitled, "Structure of the A, B, and C-Absorption Bands in KC1:T1", by A. M. Lemos, M. C. Stauber, and J. F. Marion has recently been submitted for publication in The Physical Review.

The results of the F-center investigations are described in paper (6) listed below. In this paper a set of transformations are developed which permit one to relate one set of normal co-ordinates (e.g. the set corresponding to the ground state of the F- center) to another set (e.g. corresponding to the first excited state of the F- center). These transformations can then be used to calculate the phonon broadening of the F- bands in any of the alkali halides.

The results of the KCl:Tl work are described in articles (1) through (5) listed below and in the recent article submitted to The Physical Review. In general, we have found that the absorption bands of KCl:Tl are composed of several temperature dependent subsidiary bands, and that the experimentally observed bands are simply envelopes of a rather complicated structure. We have explained the existence and behavior of these subsidiary bands for both absorption

and emission. The results of our calculations agree very well with recent experiments at Brookhaven National Laboratory. We feel that the essential problems of KCl:Tl absorption and emission have been solved.

ARTICLES:

- (1) "The B-Band in KCl-Tl", J. F. Marion and A. M. Lemos, Bull. Am. Phys. Soc., <u>14</u>, 324 (1969).
- (2) "Theoretical Analysis of the Thallium Bands in KCl", J. F. Marion and A. M. Lemos, Bull. Am. Phys. Soc., 14, 130, (1969).
- (3) "Oscillator Strength Calculations for Tl⁺ in KCl, KBr and NaCl", M. C. Stauber, A. M. Lemos, and E. A. Burke, Internal Report No. BNL 11595 for Brookhaven National Laboratory (1968).
- (4) "T1 Absorption Bands in KC1: Theoretical", M. C. Stauber, and A. M. Lemos, International Symposium on Color Centers Rome, P264, (1968).
- (5) "Oscillator Strengths for Tl⁺, M. C. Stauber, A. M. Lemos, and E. A. Burke, Bull. Am. Phys. Soc. <u>12</u>, 335, (1967).
- (6) "The General Relations Between Electron Trapping and the Normal Modes of a Lattice", A. M. Lemos, Phys. Rev. 151:2, 727, (1966).

TITLE: Thermally Stable Polymers Containing Adamantane Derivatives as Recurring Units.

PRINCIPAL INVESTIGATOR: Sung Moon

Department of Chemistry

DESCRIPTION:

In our general program of synthesizing thermally stable polymers, we chose adamantane derivatives as monomers for polymerization for two reasons. The first is that adamantane itself, which has a diamond-like structure, is known to be thermally stable. Secondly, some polymers that have been prepared by incorporating the adamantane structure were found to be stable.

We encountered difficulty in preparing 1,3-dibromoadamantane and 1,3-adamantanedicarboxylic acid according to the published methods. With some modifications, however, we were successful in preparing these monomeric materials.

We have synthesized diphenyl adamantane-1,3-dicarboxylate and have used this novel building block for preparation of a polybenzimidazole by reaction with 3,3'-diaminobenzidine. Thermal gravimetric analysis of the new polybenzimidazole indicated that the decomposition temperature of the adamantane-containing polymer (540°) was higher than that of the other polybenzimidazoles with aliphatic linkages. The new polymer, however, was not so stable as the wholly aromatic polybenzimidazoles prepared by Vogel and Marvel (J. Polymer Sci., L. 511 (1961)).

PUBLICATIONS:

S. Moon, A. Schwartz, and J. K. Hecht, "A Polybenzimidazole Containing Adamantane Units," J. Polymer Sci., in press.

STUDENT SUPPORT:

- 1. Arthur Schwartz, Doctoral student, from September 1967 to August 1970.
- 2. Howard Bohm, Doctoral Student, June 1970 to August 1970.

TITLE: Non Linear Current in a Plasma

PRINCIPAL INVESTIGATOR: Terry Morrone - Department of Physics

DESCRIPTION:

During the grant period we investigated the non linear current response of an ionized gas to an applied alternating electric field. The non linearities arise because of the velocity dependent electron neutral and ion collision frequency.

We found that the electron velocity distribution function was best described by a spherical harmonic expansion of the angular dependence. A power series expansion was developed which showed that the expansion coefficients were proportional to powers of a small parameter, the fraction of energy lost per collision. The ideas were developed in two publications. 1, 2

In a third³ we also expanded the time dependence of the distribution function and extended the work to include the effect of spatial gradients and static magnetic fields. Harmonic currents were computed under very general circumstances.

- 1. Phys. of Fluids, 10, 1507 (1967)
- 2. Phys. of Fluids, 11, 1227 (1968)
- 3. Phys. of Fluids, 11, 2617 (1968)

<u>TITLE</u>: Aeropalynological Survey in the Lower Atmosphere in the Mid-Pacific Region.

PRINCIPAL INVESTIGATOR: Leslie A. Sirkin - Department of Earth Science

DESCRIPTION:

This project was initiated in 1966 at Wallops Island, Virginia. The survey represented the initial phase of an atmosphere sampling program. It was the ultimate goal of this program to develop atmospheric monitoring systems from ground level to sub-orbital or orbital levels. The initial research utilized ground level, radio tower, ocean buoy and balloon stations with elevations ranging from ground level to 1,000 feet (the balloon stations) with intermediate stations on the Wallops Island radio mast up to 300 feet. (1)

In the survey, the dispersal of pollen from the coastal plain vegetation was monitored during the pollen rain season between March and September. Local sources of pollen were located and correlated with the pollen rain. Tagged materials were not used in the survey. Excellent recovery was achieved at all stations during peaks of pollen production, with variations in recovery associated directly with rainfall and plant pollination. Pollen data was processed by computer. (2) This means of data reduction led to the application of computer to pollen stratigraphic research. (3)

The success of the survey at low levels suggested the feasibility of extending this research first to altitudes accessible by aircraft and then to sounding rockets. Unfortunately, Wallop's Island was unable to provide the support for aircraft and rocket sampling.

Low level atmospheric sampling was conducted in liason with Dr. Eugene Holzapfel of the Bernice P. Bishop Museum in Honolulu who was studying atmospheric dispersal of insects

in the mid-Pacific region. (4) A limited number of midaltitude samples were collected and analyzed. The sampling project was suspended, however, before adequate samples could be obtained or sampling procedures perfected. Dr. Holzapfel is collecting samples from ocean vessel and will provide samples for palynologic analysis.

In conjunction with the sampling procedures, a reference of airborne pollen has been initiated. Samples of dispersed pollen have been collected in New York, Virginia, the Mid-Pacific and Alaska and are on file with the author. (5) This reference collection, although by no means complete, is intended to allow more precise identification of pollen and sources at given locations, in conjunction with standard pollen references.

Conclusions.

Some tentative conclusions may be drawn from this research.

- 1. Pollen dispersal and sedimentation generally obey Stokes Law for settling of particles, except that in the atmosphere, turbulence, convection and the natural buoyancy of pollen grains (essentially hollow microscopic spheres of 10 100/4 diameter) enables these particles to travel long distances, both horizontally and vertically.
- 2. Pollen derived from coastal plain pine and oak forests, and possibly from Piedmont forest stands, is carried into the ocean basin by air currents. While tagged pollen were not used, the presence of "exotic" pollen from known sources (such as nearby farm yard walnut trees) in offshore samples, attested to the direct atmospheric transport of such pollen a minimum of 20 miles.
- 3. Atmospheric convection, as in coastal and lagoonal "monsoon" or low pressure cells, carried pollen from herbs and grasses into the atmosphere and out to sea.

4. Where tagged materials are not used, palynologic analysis of air samples is useful in atmospheric monitoring in the lower atmosphere. This research should be extended to the upper atmosphere and to remote areas in order to enhance our understanding of the dispersal of particulate material in the atmosphere, especially in the vicinity of large metropolitan areas, forested regions and areas under cultivation.

REFERENCES:

- 1. L. A. Sirkin, 1966-1967 Aeropalynological Survey at Wallops Island, Virginia, (in manuscript); research supported by NASA multidisciplinary grant #NGL 33-001-001 (Nsg-394) and NASA Wallops Island, Virginia. The author is indebted to Wallops Island for facilities, equipment and technical and field assistance; and to Charles Grossman, undergraduate laboratory assistant on this project. See also, open file reports to the project director (11/66, 3/67, 10/67, 4/68).
- 2. L. A. Sirkin and C. Grossman, 1967, "A computer program for graphical presentation of aeropalynologic and pollen stratigraphic data", NASA, STAR, Vol. 1, No. 6.
- 3. L. A. Sirkin, 1967b, Correlation of late-glacial pollen stratigraphy and environments in northeastern U.S.A., Rev. Paleobotan. Palynol., Vol. 2, P. 205-218.
- 4. Aeropalynologic Survey in the lower atmosphere in the mid-Pacific region and over the terrestrial United States. The author is indebted to Dr. Eugene Holzapfel of the Bernice P. Bishop Museum, Honolulu, for supplying the filter samples during his atmospheric sampling project; and to Miss Mary Parthe, undergraduate laboratory assistant. (See open file reports to the project director (10/68, 3/69, 10/69, 4/70).
- 5. Reference catalog of airborne pollen. Preparations by Mary Parthe, Joseph Guidera, Kenneth Kehr, undergraduate laboratory assistants.

TITLE: Synthesis and Physical Chemical Properties of New Metal Acetylacetonates Polymers.

PRINCIPAL INVESTIGATOR: Alfred M. Vogel - Department of Chemistry

DESCRIPTION:

Efforts were made to synthesize polymers containing metal acetylacetonates and phosphorus esters. Toward this end, some monomers to be used as a backbone of the polymer have been prepared. 1-Bromo-2,4-pentanedione has been prepared and treated with aqueous copper acetate solution to yield a water-soluble chelated material. Analysis of this material showed the presence of three bromine atoms in the molecule. The spectral evidence indicated that the bromine atoms are situated on the terminal methyl groups in the molecule.

Attempts were made to convert this copper chelate to Grignard reagent by treating with magnesium, but they were unsuccessful.

Copper 2,4-pentanedione was brominated with N-bromosuccinimide, and found to be the same product prepared by brominating 2,4-pentanedione with N-bromosuccinimide and making the copper salt of this compound.

Bromination of copper ethylacetoacetate and ethylacetoacetate gave ambiguous results. When copper acetate was used as the source of copper, a blue precipitate was formed. However, when the copper salt was formed in the presence of amonium hydroxide a green precipitate resulted. The ir and nmr of these compounds were studied, but their correct structures could not be assigned.

STUDENTS SUPPORTED:

Charles Ganz, Doctoral Student, September 1966 to August 1967.

TITLE: Statistical Theory of Macromolecules.

PRINCIPAL INVESTIGATOR: Stanley Windwer, Department of Chemistry

DESCRIPTION:

One of the basic problems in the statistical theory of macromolecules is the effect of the interactions between segments far apart along the chain backbone. The net effect of this interaction is usually repulsive and hence the name "excluded volume" effect. Presently there is no exact theory of this effect.

A number of perturbation treatments have been given but only the first few terms have been calculated, and they appear insufficient.

We have investigated this problem by use of the Monte Carlo Method. The model used is that of a non-self-intersecting random walls. These walls were simulated on high speed computing devices and were examined statistically. Quantities such as the mean square end-to-end distance, the mean square radius of gyration and statistical thermodynamic functions as a function of the number of atoms in the chain can then be studied.

TITLE: Studies of Metal Solutions - Stanley Windwer

The research undertaken attempted the production of the tetramer of 1,2 dimethyoxy methane. It has been used to dissolve alkali metals to yield metal solutions. The procedure outlined below has been used so far but indicates polymerization.

Redistillation of a fraction of the tetramer was tried off clean sodium ribbon. It was found that sodium increases the rate of polymerization even in a nitrogen atmosphere;

because of this fact, sodium cannot be used as a drying agent for the tetramer.

A third preparation of the tetramer was made using 975 grams of propylene oxide and 25 grams of catalyst. A 225 ml. fraction of the tetramer was taken off a fractionating column at a head temperature of $90-94^{\circ}$ C at 2 mm of mercury. This fraction had a slight pale yellow color to it, which is indicative of the presence of polymer.

A sample of this fraction was cooled with an acetone and dry ice bath. It was then placed under vacuum and oxide free potassium, which was sealed in the system, was poured into the tetramer. A bright blue color was noticeable at the surface of the metal. This is indicative of the solavated electron system. The impurities in the tetramer caused hydrogen to be liberated. Instead of the solution becoming permeated with this blue color, it gradually darkened from pale yellow to a yellowish orange. This seemed to indicate an acceleration in the polymerization process. As the solution warmed up the rate of liberation of hydrogen had increased, indicating the expected temperature dependence.

The remaining aliquot of the tetramer was redistilled off a fractionating column at 1 mm of mercury. The distillate collected at 89-94°C had a slightly paler yellow coloration. It would seem that the rate of polymerization of the tetramer prohibits storage of the pure tetramer. A multi-redistillation of the tetramer in a closed evacuated system prior to addition of the alkali metal would be the proper method of purification.

TITLE: X-Ray Investigations

PRINCIPAL INVESTIGATOR: Alfred Zajac, Department of Physics

DESCRIPTION:

The x-ray investigations were primarily performed in two directions, namely:

- 1. Studies of anomalous transmission of x-rays through perfect crystals, and
- 2. Multiple anomalous transmission of x-rays.
- 1. Multiple Anomalous Transmission of X-rays

The <u>anomalous transmission</u> of x-rays is the transmission of x-rays by perfect crystals which are so thick that under ordinary conditions they would absorb the incident x-ray beam completely. For the anomalous transmission to occur, the beam must be incident onto a perfect crystal plate at a Bragg angle. A system of standing waves is set up within the crystal with the nodes at the atomic planes. This effectively diminishes the absorption.

The phenomenon of <u>multiple diffraction</u> occurs when more than one set of atomic planes are simultaneously inclined at the Bragg angles to one incident monochromatic x-ray beam. The combination of the multiple diffraction and of the anomalous transmission is referred to as the multiple anomalous transmission of x-rays.

Most of the results have been obtained under the supervision of Professor Alfred Zajac by Andrew Dalisa in his research work leading towards his Ph.D. degree in Physics. A technical report summarizing the theoretical and the experimental findings follows. The simultaneous anomalous transmission of x-rays has been investigated in terms of the modes of propagation of the x-ray wave field, corresponding to a special set of active wave points on the dispersion surface. One of the particular effects treated was the four field case in germanium; 0 (000), H(220), P(220) and Q(400), where 0, H, P, Q are reciprocal lattice points. By considering simultaneous anomalous transmission as a superposition of two field effects, i.e. only two beams may couple within any mode of propagation, both the intensity and polarization of each of the four beams leaving the crystal was predicted. An experimental investigation of this case has shown that this coupled pair concept provides an accurate description of the simultaneous diffraction.

The dispersion surface equation for a case of three non-negligible beams in the crystal, has been examined. It has been shown that any coplanar multiple event will result in a dispersion equation that can be factored into a product of two lower order determinants. In the general noncoplanar three field case a significant indication that the dispersion equation cannot be factored, has been presented.

The dispersion surface for a particular noncoplanar three field case: 0 (000), H(220) and P(202), has been computed. A considerable similarity to the well known two field dispersion surfaces is evident. It has also been shown that there are only a certain number of wave points, in the central region of the dispersion surface, for which anomalous transmission is possible. These special points have been shown to be identical to the set of wave points for which the modes of propagation have been calculated. Hence, this analysis of anomalous transmission, provides a complete solution to the diffraction problem, through the calculation of the <u>eigenmodes of propagation</u> of the x-ray wave field in the crystal.

The results of these investigations were presented in Moscow, USSR, during the International Crystallographic Congress in summer, 1966, and were published as:

A. L. Dalisa, A. Zajac, and C. H. Ng. "Theoretical Developments and Experiments on the Multiple Anomalous Transmission of X-Rays, Phys. Rev. <u>168</u>, 859, (1968).

Later investigations which are still in progress deal with the influence of absorption on the anomalous transmission. Tarsaim Batra is working in this field.

2. X-ray Investigations of Radiation Damage of Crystals

The change of the degree of perfection of NaClO $_3$ crystals was investigated by means of x-rays. The crystals were irradiated by various doses of gamma rays in the Brookhaven National Laboratory.

Theoretical expressions were obtained for the integrated x-ray intensities of a perfect, and of an ideal mosaic crystal (NaClO₃). These values are the extremes between which the intensities obtained experimentally from actual crystals should lie.

Three NaClO₃ crystals were used in the investigations; one unirradiated, and the other two irradiated with various doses of gamma rays. Integrated intensities for all these crystals were determined experimentally. It was found that the experimentally measured x-ray diffraction intensities became progressively larger with larger doses of gamma rays. This indicates that the effect of a stronger dose of gamma rays is to produce a more mosaic crystal.

The numerical values of the theoretical integrated x-ray intensities for perfect and for ideally mosaic NaClO $_3$ crystals were evaluated for the 002 order and for $\lambda=1.54$ A, these are $\rho_p=2.51\times 10^{-6}$ and $\rho_m=1.4\times 10^{-4}$ respectively.

We then obtained the experimental values of the absolute x-ray intensities from three NaClO₃ crystals: No. 1 unirradiated,

Nos. 2 and 3 irradiated with various dozes of gamma rays $(3 \times 10^7 \text{ and } 5 \times 10^7 \text{ respectively})$. The experimental values are: No. 1: 4.95×10^{-5} , No. 2: 1.7×10^{-4} , and No. 3: 1.0×10^{-4} . The results indicate that the degree of perfection of the unirradiated crystal is somewhere between the perfect and ideally mosaic crystal, but the gamma irradiation changes it into a mosaic crystal.

1

In one type of investigation, Laue x-ray photographs of the NaClO₃ crystals were obtained. The unirradiated crystal shows small symmetric spots, and the progressively stronger irradiated crystals showed larger spots. The crystal which received the strongest gamma dose started to show streaks on its Laue pattern, indicating greater disorder in its crystal structure.

The x-ray reflections were also recorded graphically, the results of one run are included. The ratios of the integrated intensity are:

$$I_1/I_2 = 0.538$$

and

$$I_1/I_3 = 0.287$$

We again confirmed the fact that, after the heavy dosage of gamma rays, the crystals remain single but their mosaicity increases as the gamma irradiation becomes greater.

The investigators connected with the studies of radiation damage were, George Johnson, and Kenneth Lazara.

PUBLICATIONS:

"On The Proper Modes of Propagation of X-rays", E. J. Saccocio and A. Zajac, Acta Cryst. 18, 478 (1965).

"Simultaneous Diffraction of X-rays and the Barrmann Effect", E. J. Saccocio and A. Zajac, Phys. Rev. 139, A255 (1965).

